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SEPARATION AND DETERMINATION OF INSECTICIDES BY PARTITION CHROMATOGRAPHY

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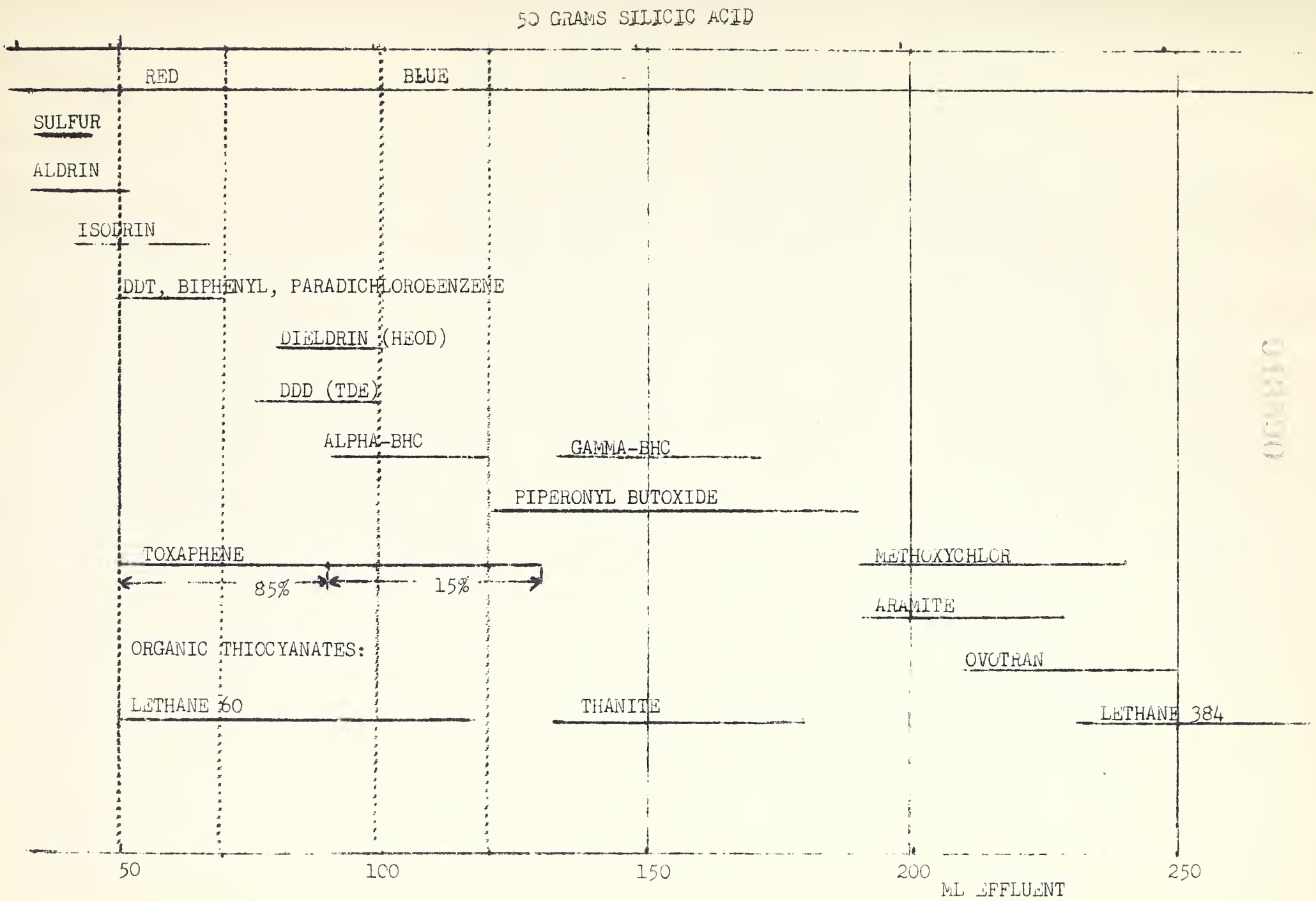
Partition chromatography has been used in our laboratory for the separation and determination of several insecticides. T. H. Harris in his paper "Partition Chromatography in Analysis of Insecticide Formulations," Advances in Chemistry Series, Number 1, page 266 (1950), gave applications of the method to gamma-benzene hexachloride, DDT, and methoxychlor. The procedure for gamma-benzene hexachloride is an official method in the Methods of Analysis of the Association of Official Agricultural Chemists. The column used for the separation is prepared with nitromethane on a supporting medium of silicic acid, and with hexane saturated with nitromethane as the mobile solvent. The chromatographic properties of several insecticides have been charted to extend the applicability of this procedure. B. L. Samuel of the Division of Chemistry, Commonwealth of Virginia, submitted some of these data in chart form giving the properties found in his laboratory.

The chromatographic properties of these insecticides depend partly on the preparation of the column, in particular on the properties of the silicic acid used. Therefore the chart gives only the approximate positions of the various insecticides, although the relative positions are useful in the application of the method.

Partition chromatography has been found most useful for the separation of the following mixtures:

DDT, Dieldrin (HEOD)	75 gram column
DDT, DDD	100 gram column
DDT, Gamma-BHC	100 gram column
DDT, Methoxychlor	
Aramite in various mixtures	
Ovotran in various mixtures	

The separation of DDT from technical aldrin is not considered satisfactory. Most solvents appear with the red dye although some solvents may contaminate other fractions.


50 GRAMS SILICIC ACID
RED
BLUE
SULFUR
ALDRIN
ISODRIN
DDT, BIPHENYL, PARADICHLOROBENZENE
DIELDRIN (HEOD)
DDD (TDE)
ALPHA-BHC
GAMMA-BHC
PIPERONYL BUTOXIDE
TOXAPHENE
85%
15%
METHOXYCHLOR
ARAMITE
ORGANIC THIOCYANATES:
OVOTRAN
LETHANE 60
THANITE
LETHANE 384
50
100
150
200
250
ML EFFLUENT

TOTAL ARSENIC IN ANT POISON SOLUTIONS OF SODIUM ARSENITE OR SODIUM ARSENATE CONTAINING APPROXIMATELY 1.2% ARSENIC

Transfer 4 - 6 g of sample to a 500 ml Kjeldahl digestion flask and add with caution 6 - 8 ml of concentrated sulfuric acid and 2 ml of nitric acid. Heat over a low flame until the mixture begins to darken and then add a few drops of fuming nitric acid (or a small quantity of conc. nitric acid). Continue the additions of nitric acid and heating until all organic matter is destroyed and the nitric acid is driven off as shown by the appearance of dense white fumes of sulfuric acid. Cool, add in small portions down the side of the flask about 50 ml of water (to decompose any nitrosylsulphuric acid formed), and heat after each portion of water added until all nitric oxide fumes are expelled.

Cool and transfer to a 500 ml Erlenmeyer flask, dilute with water to 100 ml, add 1 g of potassium iodide, heat to boiling, and evaporate to about 40 ml (not less). Cool, dilute to 150 - 200 ml, and remove the excess of iodine with 0.05 N sodium thiosulphate. If the solution is slightly colored from organic matter or from any other cause other than free iodine, add the thiosulphate until it is nearly colorless, then a few drops of starch indicator, and continue adding the thiosulphate slowly until the blue color just disappears.

Neutralize with sodium bicarbonate (should be added in small portions to prevent excessive foaming), add 4 - 5 g in excess and then 0.05 N iodine solution from a buret, shaking the flask continuously, until the yellow color disappears slowly from the solution. Then add 5 ml of starch solution and continue adding the iodine solution, drop by drop, until a permanent blue color is obtained.

Calculate the percentages of total arsenic and sodium arsenite or arsenate on the basis that

1 ml 0.05 N I is equivalent to - 0.001873 As
- 0.003248 $NaAsO_2$
- 0.004648 Na_2HASO_4

COLORIMETRIC DETERMINATION OF CHROMIUM IN DUSTS

REAGENTS

a) Fusion mixture. Mix 3 g of sodium nitrate with 20 grams of anhydrous sodium carbonate.

b) Potassium dichromate (Reagent standard, National Bureau of Standards)

PROCEDURE

For a sample containing about 0.5% of chromium, mix 0.5 g of sample with 3 grams of fusion mixture and fuse in a platinum crucible. Extract the melt with hot water, filter through asbestos in a Gooch crucible and make the filtrate to volume in a 200 ml volumetric flask. Determine the absorbance of this solution at 400 millimicrons in a 1 cm cuvette with a Beckman spectrophotometer, model DU.

For the standard, dissolve 0.2 g potassium dichromate (b) in 200 ml water, dilute 20 ml of this solution to 100 ml in a volumetric flask, transfer 20 ml of the diluted solution to a 100 ml volumetric flask, add 1½ g fusion mixture and make to volume. This solution contains 14.14 micrograms/ml of chromium and the same concentration of fusion mixture that was used in preparing the sample. A solution of fusion mixture containing 3 grams in 200 ml is used as the blank.

Calculate the percentage of chromium in the sample from the absorbances for the sample and the standard.

NOTES: 1. The maximum absorbance for sodium chromate is at 373 millimicrons, but at 400 millimicrons the background absorbance is much less. For samples containing water-soluble chromates the sample and standard solutions may be prepared to contain 0.1 N sodium hydroxide and ca 6 micrograms/ml of chromium, and the absorbances measured at 373 millimicrons.

2. In the presence of manganese add a few drops of ethyl alcohol to the dissolved melt in order to reduce the sodium manganate. Uranium interferes.

REFERENCE: Hillebrand, Lundell, Bright, and Hoffmann, "Applied Inorganic Analysis", p. 530 (1953).